Enhancing T_c in ferromagnetic semiconductors

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We theoretically investigate disorder effects on the ferromagnetic transition ("Curie") temperature T_c in dilute $III_{1-x}Mn_xV$ magnetic semiconductors (e.g., $Ga_{1-x}Mn_xAs$) where a small fraction ($x \approx 0.01-0.1$) of the cation atoms (e.g., Ga) are randomly replaced by the magnetic dopants (e.g., Mn), leading to long-range ferromagnetic ordering for $T < T_c$. We find that T_c is a complicated function of at least eight different parameters including carrier density, magnetic dopant density, and carrier mean free path; nominally macroscopically similar samples could have substantially different Curie temperatures. We provide simple physically appealing prescriptions for enhancing T_c in diluted magnetic semiconductors and discuss the magnetic phase diagram in the system parameter space.

Diluted magnetic semiconductors (DMS), which are ferromagnetic for $T < T_c$, are of great fundamental interest because they provide an example of interplay among magnetism, disorder, carrier dynamics, and transport properties. Starting with the early report of carrier-induced global ferromagnetism in $In_{1-x}Mn_xAs$ (Ref. 1) and later[2] in $Ga_{1-x}Mn_xAs$, with the typical magnetic impurity concentration $x \approx 5\%$, there have been many studies reporting ferromagnetism in DMS systems as disparate as $Ga_{1-x}Mn_x$,[3] $Ga_{1-x}Mn_xN$,[4] $Ga_{1-x}Mn_xP$,[5] TiO_2-Co,[6] SnO_2-Co,[7] and ZnCrTe (Ref. 8) among others. There is a great deal of current research activity in the subject, and different DMS materials with different magnetic properties are likely to continue appearing in the near future. In spite of this enormous activity, there is no current consensus on the basic magnetic model underlying DMS ferromagnetism, particularly in the presence of disorder, which is always present.[9] Experimentally the situation turns out to be quite complex as the ferromagnetic properties (in particular, the Curie temperature T_c) seem to depend very sensitively[10] on the materials growth and processing (e.g., annealing) conditions, and T_c in nominally identical samples could differ substantially depending on the precise details of sample preparation and processing.

In this Rapid Communication, we develop a theory for the prediction of T_c in DMS systems by focusing on the most-studied DMS system, viz., $Ga_{1-x}Mn_xAs$, as a function of various system parameters (to be discussed below). Our work, which includes spatial disorder of the system (by virtue of the random locations of the magnetic Mn atoms), leads naturally to the conclusion that T_c is a complicated (and in general unknown) function of the system parameters; the number of independent variables (at least eight as discussed below) determining T_c, even within the minimal zeroth order effective Hamiltonian approach, are sufficiently large that nominally macroscopically identical samples may very well have significant variations in T_c, as is indeed observed. Some of the system parameters (e.g., the nature of spatial disorder, various defects present in the real samples, the impurity scattering potential, etc.) are generally unknown as a matter of principle, and therefore a precise quantitative prediction for T_c as a function of the *known* system parameter (i.e., the Mn concentration x and the carrier density n_c), as is often done in the literature, could be quite meaningless because the same values of x and n_c may lead to different T_c values in different

samples, depending on the details of various defects, impurities, and/or disorder in the system (which can be influenced, for example, by sample annealing). Among the various possible defects, As antisites and Mn interstitials are known to be important. In addition, likely correlated clustering of Mn atoms (instead of uncorrelated random positioning at Ga sites) is also thought to be significant.[11] Experimentally, a strong dependence of T_c on the sample conductivity has been found with T_c typically increasing with conductivity; samples with the highest (lowest) conductivity invariably have the highest (lowest) T_cs, but whether this dependence arises entirely from the higher conductivity samples having higher carrier densities (as is commonly assumed in the literature) or longer mean free paths (MFP) (or equivalently, higher mobility) or a combination of the two is presently unknown. We therefore see that $T_c \equiv T_c(n_i, n_c, l, J_0; N_{AS}, N_I, N_C, J_{AF} \cdots)$ is a function of at least eight different parameters due to the complexity of the problem. The three obvious parameters, which have been discussed widely in the literature, are the active magnetic moment density n_i due to substitutional Mn dopants, the carrier density n_c, and the carrier MFP l (as obtained from the dc conductivity), and in this paper we mostly focus on the dependence of T_c on these three parameters. The other relevant parameters, e.g., N_{AS} (the As antisite defect density), N_I (the Mn interstitial defect density), N_c (a set of parameters defining the clustering of Mn atoms or the correlation in their spatial positions), and J_{AF} (the direct short-range Mn-Mn antiferromagnetic exchange interaction), are quantitatively important, but essentially unknown (either experimentally or theoretically), and their explicit inclusion in the theory for a quantitative comparison with the experimental results is hence not particularly useful. However, we assume that the influence of these parameters can be included qualitatively in the theory by appropriately adjusting the parameters n_i, n_c, l, and most importantly, the effective ferromagnetic coupling strength J_0 which sets the overall energy scale in the problem since we express T_c in the units of J_0. We find that even with just three independent parameters (n_i, n_c, l), the problem is quite rich, leading to many subtle possibilities.

We use the standard Ruderman-Kittel-Kasuya-Yosida (RKKY)–Zener effective magnetic model[12] for describing the coupled carrier-local moment system since we are interested in the so-called "metallic" DMS regime with itinerant

carriers where T_c is maximized. (The insulating strongly localized DMS regime can also be ferromagnetic, but the nature of the insulating DMS ferromagnetism, with typically rather low T_c, is fundamentally different[13] from the metallic regime with higher T_c being considered in this paper.) We note that while it is somewhat crude to characterize the metallic DMS regime by a MFP l extracted from the conductivity $\sigma = n_c e^2 \tau / m_c$ (and $l = v_F \tau$, where τ is the transport relaxation time, m_c the carrier mass, and v_F the carrier Fermi velocity), the extracted value of the MFP l is rather short (typically around one to a few lattice constants). We employ an effective magnetic model Hamiltonian[14] for interacting impurity moments where the carrier degrees of freedom have been integrated out

$$H = \sum_{i,j} J_F(\mathbf{r}_{ij})\mathbf{S}_i \cdot \mathbf{S}_j + \sum_{i,j}' J_{AF}\mathbf{S}_i \cdot \mathbf{S}_j, \qquad (1)$$

where the subscripts F (AF) denote the ferromagnetic (antiferromagnetic) part of the impurity spin ($\mathbf{S}_i$) interaction and the prime in the second term implies that the sum is restricted to nearest neighbors since the short-range antiferromagnetic interaction only couples nearest-neighbor Mn atoms (if there are any). We do not explicitly include the direct antiferromagnetic exchange term in the results shown in this paper, assuming without any loss of generality (within our theoretical scheme) that J_{AF} effectively modifies (in fact, reduces) the carrier-mediated ferromagnetic interaction. Since the interaction strength is the basic energy parameter in our effective magnetic Hamiltonian, it makes little sense to keep two unknown coupling parameters. We write Eq. (1) with the direct antiferromagnetic exchange term for our general qualitative discussion of the DMS phase diagram as described below.

The first term in Eq. (1), the carrier-mediated ferromagnetic interimpurity interaction, is of the RKKY form in our effective model: $J_F(r) = J_0[(2k_F r)\cos(2k_F r) - \sin(2k_F r)]/(k_F r)^4$, where J_0 is the fundamental ferromagnetic coupling parameter in the problem (which implicitly includes all materials and band structure information about the system), and k_F the carrier Fermi momentum (and $r = |\mathbf{r}_{ij}|$ the spatial separation between randomly located substitutional Mn pairs in the GaAs lattice). We note one important feature of $J_F(r)$: for high carrier density, $n_c \gg n_i$, the oscillatory aspects of the RKKY interaction come into play, potentially suppressing DMS ferromagnetism—the details of this suppression are an important topic of this work. A straightforward Weiss mean-field treatment of the RKKY interaction, neglecting all spatial disorder effects and assuming a continuum virtual crystal approximation (VCA), was first carried out a long time ago (and has recently been rediscovered in the DMS context) leading to $T_c^{VCA} \propto n_i n_c^{1/3}$. This T_c^{VCA} (with appropriate quantitative modifications arising from band structure effects) has been extensively (and uncritically in our view) used in the DMS literature for explaining and predicting T_c in DMS systems. In the current work we include in our calculation of T_c spatial disorder (thus relaxing the continuum VCA) and finite MFP, which are both significant in DMS materials. We carry out a direct numerical calculation of T_c on the GaAs lattice treating the random disorder of Mn spatial positions *exactly* in the theory.[14]
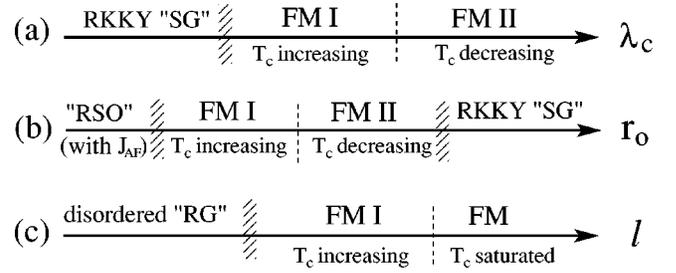
FIG. 1. DMS phase diagram. Note that the dashed lines between FM phases are *not* phase transition.

First we qualitatively discuss the DMS phase diagram as a function of the variable n_i, n_c, and l, noting that the standard VCA implies that the system is a ferromagnet for *all* values of n_c and n_i with T_c^{VCA} increasing monotonically with increasing impurity (n_i) and carrier (n_c) density. It is essential to include MFP effects in the theory. The RKKY interaction has been calculated in the presence of resistive scattering earlier in the literature,[15] and the modified RKKY interaction in the presence of a finite MFP l has the form $J_F(r;l) = J_F(r)$ for $r \ll l$ and $J_F(r;l) = J_0 \cos[\phi(r)]/(2k_F r)^3$ for $r \gg l$, where $J_F(r)$ is the standard RKKY formula and $\phi(r)$ is a completely random function of r. The inclusion of short-range direct antiferromagnetic exchange [Eq. (1)], RKKY oscillation, and transport MFP effects permits us to obtain the qualitative $T = 0$ DMS phase diagram as a function of three length variables $\lambda_c \sim n_c^{-1/3}$; $r_o \sim n_i^{-1/3}$; l. The schematic phase diagram depicted in Fig. 1 assumes λ_c, r_o, and l to be completely independent variables (which they cannot be in real systems). In each case shown in Fig. 1, we assume the other variables to be *fixed* at some reasonable "optimum" values (which may not always be experimentally possible).

In Fig. 1(a) the system is an RKKY spin-glass (SG) system at very small values of λ_c (equivalently very large values of n_c). This arises from the frustration induced by the RKKY oscillations which are dominant in the high k_F ($n_c \gg n_i$) limit (but are essentially absent in the dilute $n_c \ll n_i$ limit). As λ_c increases (i.e., $n_c \sim \lambda_c^{-3}$ decreases), the RKKY SG phase gives way to a ferromagnetic phase. The Curie temperature of this phase increases with decreasing density until the optimum T_c is reached, after which T_c begins to decrease with decreasing carrier density. In Fig. 1(b) we depict the DMS phase diagram in magnetic impurity density n_i ($\sim r_o^{-3}$) assuming l and λ_c to be fixed at reasonable optimal values. For small r_0 (large n_i) the nearest-neighbor direct antiferromagnetic exchange between the Mn moments becomes important and competes with the carrier-induced RKKY interaction, leading to a random spin-ordered (RSO) nonferromagnetic phase (which may or may not be a SG phase). For larger r_0 we enter the ferromagnetic phase with T_c (r_0) similar to the T_c profile in Fig. 1(a); eventually we find a phase transition to the RKKY SG phase for very large r_0 where $n_c \gg n_i$. Thus, except for the antiferromagnetic exchange induced RSO phase in the high impurity concentration limit in Fig. 1(b), the phase diagrams of Figs. 1(a) and 1(b) are essentially mirror images of each other as one shifts from $n_c \gg n_i$ ($n_i \gg n_c$) to $n_c \ll n_i$ ($n_c \gg n_i$) in Fig. 1(a) [1(b)], respectively. Finally, in Fig. 1(c) we discuss the phase diagram as a function
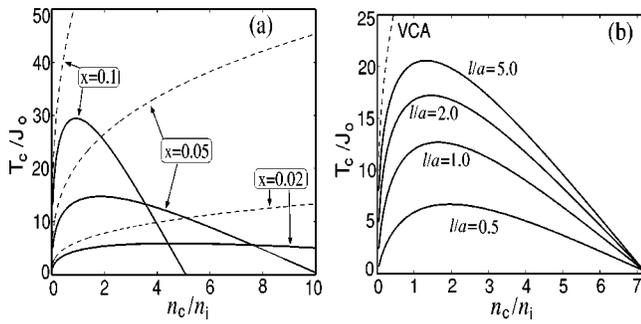
FIG. 2. Calculated T_c (solid lines) as a function of n_c/n_i (a) for different x values and fixed MFP $l/a=5$, and (b) for different MFP l/a and fixed $x=0.07$. Dashed lines indicate the results from VCA.

FIG. 3. Calculated $T_c(l)$ for different n_c/n_i and fixed $x=0.07$. Note $T_c^{VCA}/J_0=32.6,41.6,52.2,63.1$ for $n_c/n_i=1,2,4,7$, respectively.

of the MFP for fixed n_i and n_c values. For very small l, the carrier-induced ferromagnetic RKKY coupling is suppressed, and the interimpurity interaction has random sign, leading to a type of (non-RKKY) disordered random glassy (RG) non-ferromagnetic ground state which, with increasing l, should make a phase transition to the ferromagnetic phase. As one increases l further the ferromagnetic phase should initially be enhanced (i.e., T_c rises with l) with an eventual saturation of T_c determined by the precise values of n_c and n_i. Thus it is readily evident that the best technique to enhance T_c would be to increase the MFP sitting at fixed optimal values of n_c and n_i. Although this is perfectly reasonable as a matter of principle, it may be difficult to increase the MFP without affecting n_c and n_i.

Following this qualitative introduction to the DMS phase diagram on the basis of the simple effective Hamiltonian approach, we now consider the quantitative dependence of $T_c(n_c,n_i,l)$ in DMS systems focusing on the well-studied $Ga_{1-x}Mn_xAs$ system. To do this we carry out a thermal lattice mean field treatment (treating exactly the spatial disorder of random Mn locations at Ga substitutional sites in the zinc-blende GaAs lattice) of the effective Hamiltonian as described in Ref. 14. Such a treatment avoids the physically unrealistic assumptions of the continuum VCA involved in deriving T_c, and should be an excellent approximation for obtaining T_c because of the very large coordination number in the fcc zinc-blende GaAs lattice structure. As emphasized previously, this lattice mean field theory (LMFT) can essentially be carried out for infinite size systems, thus avoiding the finite size complications inherent in direct Monte Carlo simulations which are *not* particularly well suited for rapidly determining T_c.

In Fig. 2 we present our theoretical results for $T_c(n_c,n_i,l)$. As noted earlier, we have ignored the direct short-range antiferromagnetic exchange interaction in obtaining these results. We also ignore interstitial defects (and antisite As) in this calculation; we assume that n_i and n_c are the *effective* active local moment and hole density, respectively, which already incorporate various defect effects.

In Fig. 2(a) we show the calculated T_c as a function of n_c/n_i for several values of x in a "highly" metallic system ($l/a=5$, where a is the GaAs lattice constant), whereas in Fig. 2(b) we show $T_c(n_c/n_i)$ for a fixed value of x (=0.07) but for several different values of l/a. We show the simple continuum VCA result in each case for the sake of comparison.
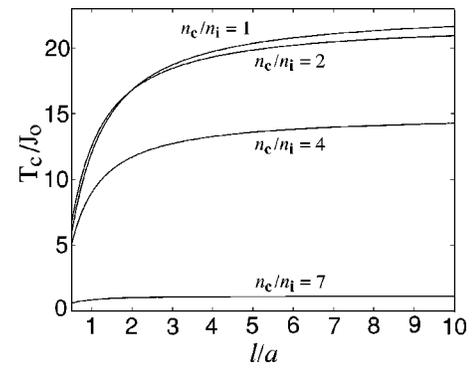
It is obvious that the simple theory of T_c^{VCA} is qualitatively incorrect for large n_c/n_i where T_c actually reaches a maximum and then decreases with increasing carrier density (due to the frustration inherent in the RKKY oscillations playing a role for $n_c/n_i>1$ or equivalently $k_Fr_0>1$) in contrast to the erroneous claim (made extensively in the literature) that $T_c(n_c)\propto n_c^{1/3}$ (as obtained from continuum VCA) would continue increasing monotonically with carrier density. It is, however, important to note that our results presented in Fig. 2 indicate a fairly large regime of (qualitative and even semi-quantitative) validity of the simple VCA with the appropriate numerical modification of J_0 which is an adjustable parameter merely setting the scale of energy in our theory. In particular, the simple VCA theory remains valid up to $n_c/n_i \sim 0.5$, and perhaps even up to $n_c/n_i \sim 1.0$, depending on the Mn content (i.e., x). The optimum n_c/n_i value where T_c is maximum decreases as the Mn concentration increases, and this indicates that, for a given value of the effective coupling J_0, T_c cannot really be arbitrarily increased just by increasing the carrier density (although increasing carrier density by co-doping with nonmagnetic impurities[16] should enhance T_c somewhat), but typically T_c is optimum for $n_c/n_i \sim 1$. This suggests that the current popular wisdom of trying to enhance T_c for GaMnAs (and other DMS materials) simply by increasing carrier density would not work much beyond $T_c \sim 300$ K (since the current maximum T_c is around 170 K).

Our results for $T_c(l)$ presented in Fig. 3 indicate one possible strategy for enhancing T_c. As can be seen in Fig. 3, T_c increases monotonically with increasing MFP, eventually saturating at the maximum possible T_c for a given value of n_c/n_i (which is somewhat below the corresponding T_c^{VCA}). Thus a clear strategy to enhance T_c is to optimize n_c/n_i for a given Mn content such that one is at or near the optimum carrier density (i.e., near the maximum in Fig. 2), $n_c/n_i \sim 0.5-2$, depending on x, and then to enhance the carrier MFP by reducing scattering effects through a systematic improvement of sample quality. Experimentally, it is now established[17] that enhancing conductivity by improving sample quality (e.g., via annealing) can substantially increase T_c, but the conductivity σ depends both on the carrier density n_c and the MFP l, and it has almost universally been assumed that the increase of T_c due to enhanced σ arises entirely from the increasing carrier density, whereas we find that T_c im-
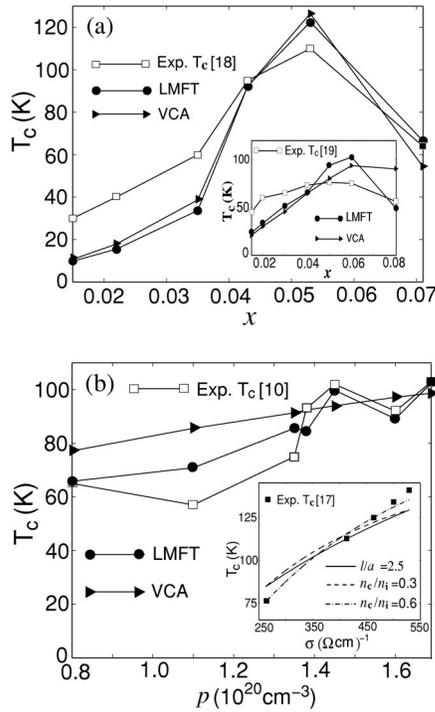
FIG. 4. (a) Comparison of T_c with the experimental results of Refs. 18 and 19 (inset) as a function of x. (b) Comparison of T_c with the experimental results of Ref. 10 as a function of hole density and those of Ref. 17 as a function of conductivity (inset). The only "free" parameter for the fit is the value of exchange coupling which is taken to be a constant.

provement arises both from increasing n_c and l.

Finally, in Fig. 4 we show a direct comparison between our theory and recent GaMnAs experimental results from several different groups.[10,17–19] For each set of results in Fig.

4 we have extracted $T_c[n_c, n_i, \sigma(l)]$ from the relevant experimental work as described in the figure captions. It is obvious that the experimental results are well described by the theory; the agreement can be made essentially exact by slightly adjusting n_i and/or by choosing slightly different J_0 for different values of x, both of which may be reasonable since Mn interstitials (whose density may very well be a function of x) are likely to affect the value of effective coupling by modifying the number of active Mn moments participating in global ferromagnetism and by introducing some direct Mn-Mn antiferromagnetic exchange coupling. It is also evident from Fig. 4 that the continuum VCA, while qualitatively reasonable in some regimes of the parameter space, does not provide a good quantitative description for the experimental results. We mention that our neglect of the complicated valence band structure of GaAs in the theory is a simplification that should not affect our conclusions in any essential way since band structure effects enter our theory only through various parameters such as J_F, J_{AF}, l, n_c, and n_i.

In conclusion, we have discussed the DMS phase diagram, taking into account effects of carrier-mediated ferromagnetic and antiferromagnetic coupling between the impurity moments as well the frustration arising from the RKKY oscillations, finding that ferromagnetism is only one of four distinct magnetic phases possible in the disordered system. We have also carried out a detailed theoretical T_c calculation as a function of magnetic impurity concentration, carrier density, and conductivity (i.e., MFP), including full effects of spatial disorder and randomness, finding that the maximum T_c is obtained for an optimum carrier density $n_c/n_i \sim 0.5-2$, depending on the Mn concentration. We have shown that for T_c to be enhanced at given values of n_c and n_i, one needs to increase the MFP as much as possible.

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